

## Articles

# Two Photoelectrochemical Processes for TiO<sub>2</sub> Electrode under UV Illumination

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TiO<sub>2</sub> thin film electrode was prepared by a sol-gel method on ITO substrates. Cyclic voltammetric behavior of the ITO/TiO<sub>2</sub> electrode under ultraviolet (UV) illumination was investigated in the solution of Na<sub>2</sub>SO<sub>4</sub>. There are two photoelectrochemical processes for TiO<sub>2</sub> electrode under UV illumination. One is a fast process, which results in the appearance of anodic photocurrent. The anodic photocurrent will appear and disappear with the light on and off. The other is a slow process, which will be responsible for the appearance of an oxidative peak. When the electrode is illuminated under UV light for a long time, a new oxidative peak can be observed. The peak current increases with the increase of UV illumination time. It is assumed that the new peak belongs to the oxidation of Ti<sup>3+</sup>, which formed and accumulated on the electrode surface during the UV illumination. A detailed mechanism is proposed on the base of these two photoelectrochemical processes. It is assumed that the change of hydrophilicity of TiO<sub>2</sub> thin film may be related to the slow process while the film irradiated by UV light.

**Keywords** TiO<sub>2</sub> electrode, UV illumination, cyclic voltammetry, hydrophilicity

## Introduction

Titanium dioxide has been investigated intensely as a well-known semiconducting photocatalyst for its potential application in many areas such as the treatment of wastes and pollutants in air or water<sup>1,2</sup> and in solar cells.<sup>3,4</sup> After the report of photo-induced hydrophilicity of TiO<sub>2</sub>,<sup>5</sup> its applications were extended to a larger range including anti-fogging glass and self-cleaning construction materials. Many experimental results have verified the fact that the UV irradiation of TiO<sub>2</sub> thin film can produce a highly hydrophilic surface.<sup>6-10</sup> The water contact angle can be exhibited nearly zero degree after the UV illumination for enough time. X-Ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) measurements can detect the signal of Ti<sup>3+</sup> for the UV irradiated surface of TiO<sub>2</sub>.<sup>10</sup> In fact, electrochemical methods are very effective

to detect the charge transfer and the formation of electroactive species. But the *in-situ* electrochemical measurements are very rare for TiO<sub>2</sub> electrode under UV light illumination. In the present paper, the behavior of ITO/TiO<sub>2</sub> electrode under illumination is studied by cyclic voltammetry method. It is found that there are two photoelectrochemical processes for TiO<sub>2</sub> electrode under UV illumination. One is a fast process, which results in the appearance of anodic photocurrent. The other is a slow process, which will be responsible for the formation and accumulation of Ti<sup>3+</sup>, and bring on the appearance of a new oxidative peak in the cyclic scan. Based on the experimental results, it is assumed that the changes of hydrophilicity of the films may be related to the slow process, which is the formation and accumulation of Ti<sup>3+</sup> on the surface when the film irradiated by UV light.

## Experimental

### *Electrochemical measurements*

The electrochemical measurements were carried out in a conventional three-electrode, single-compartment glass cell, fitted with a quartz window. The ITO/TiO<sub>2</sub> thin film electrode served as the working electrode. The auxiliary electrode was a Pt flat with a large area (about 20 times that of the working electrode). A saturated Hg-HgCl<sub>2</sub> electrode (SCE), connected through a Luggin capillary, was used as the reference electrode. All the potentials reported in this paper are given with respect to SCE. The measurements carried out in a sodium sulfate solution (0.5 mol·L<sup>-1</sup>, pH = 6.6) after being deaerated by bubbling with N<sub>2</sub>. Reagents were of analytical grade. The solutions were prepared by deionized water. All experiments were carried out at room temperature [(298 ± 1) K]. The ITO/TiO<sub>2</sub> electrode area is 0.5 cm<sup>2</sup>, which is estimated by its geometric dimension.

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### Apparatus

The cyclic voltammetric curves were measured by using a CHI-660 electrochemistry work station. A UV light (253.7 nm) was employed as the excitation light source. UV illumination was carried out using a 8-W ultraviolet lamp with a wavelength of 253.7 nm. The light intensity was measured by an ultraviolet photometer (Beijing Normal University).

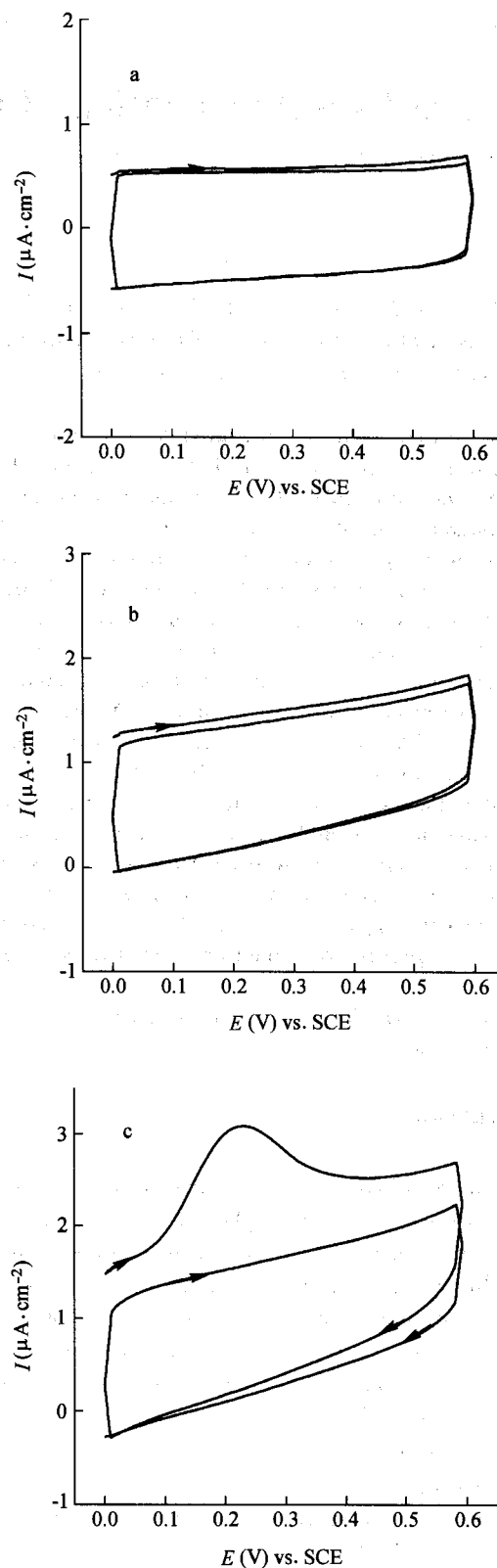
### Electrode preparation

The ITO/TiO<sub>2</sub> electrode was prepared by a sol-gel method. The thin film was annealed at 450 °C in air for 1 h which resulted in TiO<sub>2</sub> anatase films with a thickness of about 100 nm. The XRD measurements confirm the formation of TiO<sub>2</sub> anatase films after the heat treatment. The SEM observation shows that the nanoscale thin film of TiO<sub>2</sub> was composed of nanoparticles of TiO<sub>2</sub> with 50–100 nm and some nanoscale holes between the nanoparticles. The thin film electrode was fabricated by attaching a copper wire using silver paste. An epoxy was used to cover the electrode except for the tested TiO<sub>2</sub> surface.

### Results and discussion

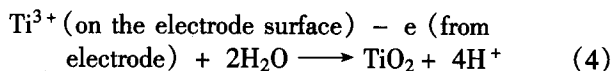
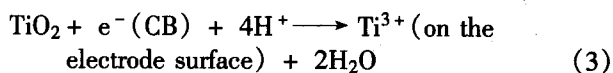
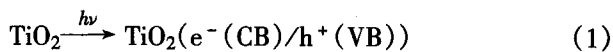
Fig. 1(a), (b) and (c) show the cyclic voltammograms for the TiO<sub>2</sub> thin film electrode in the dark (Fig. 1(a)) and under UV irradiation for different illumination time respectively. The anodic photocurrent was observed immediately when the electrode was exposed to light as shown in Fig. 1(b). It is reasonable to observe the anodic photocurrent, because TiO<sub>2</sub> is *n*-type semiconductor, and it is a typical characteristic to show anodic photocurrent. In this point, it is consistent with the report of literature.<sup>8</sup> The anodic photocurrent will disappear when the light is off. This fact reflected that the appearance of anodic photocurrent was related to a transient process. An obvious charge and discharge current can be observed which indicated the characteristic features for the thin film electrodes.

When the TiO<sub>2</sub> electrode is irradiated for a long time, such as 30 min, a new oxidative peak appears in the first scan besides the anodic photocurrent as shown in Fig. 1(c). However, The amplitude of this peak decreases significantly when a second cyclic potential scan is performed directly afterward, which reveals that the new species is not stable enough and disappears after the anodic polarization in the first scan. It is also found that the peak current is proportional to the illumination time. When the illumination time duration increases, the peak current will increase. This result reveals that the oxidative peak was related to photo-induced species. It is assumed that the photo-induced species is Ti<sup>3+</sup>, which formed and accumulated on the electrode surface during the illumination. The peak resulted from the re-oxidation of photo-induced Ti<sup>3+</sup>.<sup>11</sup>



**Fig. 1** Cyclic voltammograms for the ITO/TiO<sub>2</sub> thin film electrode in a solution containing 0.5 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> (pH = 6.6) in the dark (a) and under a 253.7 nm UV light irradiation (0.2 mW/cm<sup>-2</sup>) for 5 min (b) and 30 min (c).

The involved reactions are shown as below:



This mechanism can account for the voltammetric results. Because  $\text{TiO}_2$  is a semiconductor with a band gap of about 3.0 eV, UV light (with a wavelength shorter than ca. 400 nm) can excite pairs of electrons and holes. When the electrode is illuminated by UV light, electrons and holes can be produced on the surface of  $\text{TiO}_2$ . The anodic photocurrent results from Eqs. (1) and (2), which are fast process. At the same time, there is a slow process which involves the formation and accumulation of  $\text{Ti}^{3+}$ . The photogenerated electrons reduced  $\text{TiO}_2$  to form  $\text{Ti}^{3+}$  according to Eq. (3). The photo-induced  $\text{Ti}^{3+}$  re-oxidized on the electrode surface to show oxidative peaks (Eq. (4)). The key factor for the formation of  $\text{Ti}^{3+}$  may be the light sources besides the illumination time. In our experiments, an UV light with a wavelength of 253.7 nm was used. The UV light with shorter wavelength can give higher energy electrons which can cause the happening of reaction (3). Then,  $\text{Ti}^{3+}$  produced and piled up on the surface when the electrode was irradiated by UV light. Therefore, an oxidative peak resulted from photo-induced  $\text{Ti}^{3+}$  can be observed after a long time illumination.

Fig. 2 shows the time dependence of water contact angle of the  $\text{TiO}_2$  film on ITO upon UV illumination. The thin film yields a contact angle of approximately  $30^\circ$  before exposed to UV light. With the UV illumination, the water contact angle of the film decreased, which means that the film converted to a hydrophilic state. Correspondingly,

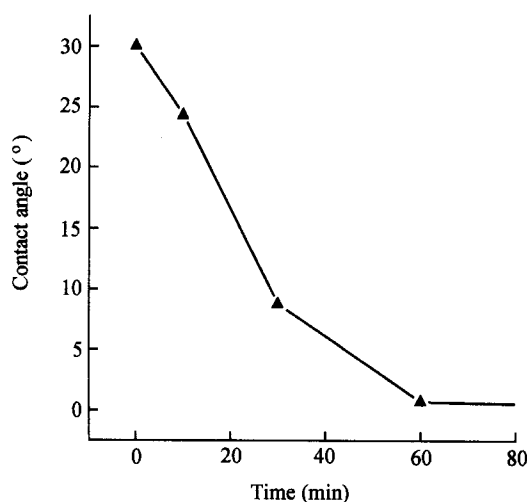


Fig. 2 Water contact angle changes of the ITO/ $\text{TiO}_2$  thin film under illumination of ultraviolet light.

there is an increasing tendency with the illumination time for the current of the photo-induced oxidative peak as shown in Fig. 3. Comparing Fig. 2 with Fig. 3, it can be seen that there is a same tendency between the change of hydrophilicity and the peak current. The larger the peak current, the more hydrophilic state the film. It is assumed that the change of hydrophilicity of  $\text{TiO}_2$  film could be related to the formation and accumulation of  $\text{Ti}^{3+}$  on the surface when the film was irradiated by UV light. More details are under way in our laboratory.

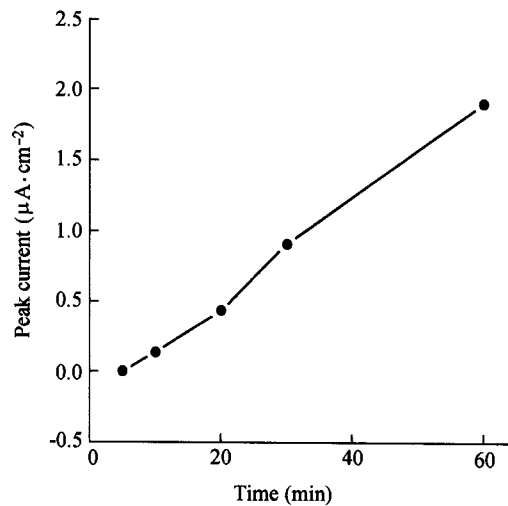


Fig. 3 Dependence of photo-induced peak current of cyclic voltammograms with the illumination time.

## Conclusions

The cyclic voltammetric behavior of the ITO/ $\text{TiO}_2$  electrode under UV illumination is reported in this paper. Two photoelectrochemical processes can be distinguished for  $\text{TiO}_2$  thin film electrode under UV illumination. One is a fast process, which resulted in the appearance of the anodic photocurrent. The other is a slow process, which will be responsible for the appearance of a photo-induced oxidative peak. It is assumed that the change of hydrophilicity of the films may be related to the slow process on the surface when the film was irradiated by UV light.

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